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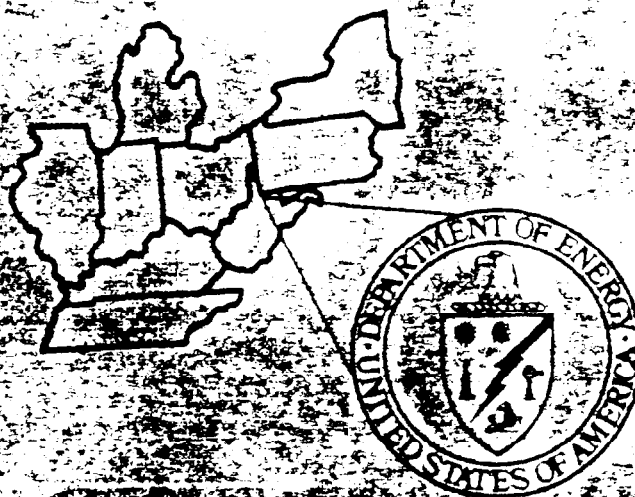University of Kentucky/Department
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EXCHANGEABLE CATIONS IN THE
DEVONIAN SHALE SEQUENCE

by

H.B. Maynard and R. Ulmschneider

FOSSIL ENERGY

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for

Morgantown Energy Research Center
Morgantown, West Virginia 26505

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EXCHANGEABLE CATIONS IN THE DEVONIAN SHALE SEQUENCE

ERDA Topical Report ORO-5201-1

by

J. B. Maynard[1] and R. Ulmschneider[2]

ABSTRACT

Because exchangeable cations may affect a shale's ability to transmit fluids and its response to some fluids used in fracturing or drilling, a study of the exchangeable cations in core samples from the Ohio Black Shale in Richland County, Ohio, and Perry County, Kentucky, was undertaken. Na^+ is the cation usually associated with fluid problems, but it is generally low in the samples tested, so that problems related to ion-exchange are unlikely to occur.

An unexpected analytical problem was encountered. A few percent of a carbonate mineral in a sample severely interferes with the cation determination by releasing Ca^{++}. Almost all of our samples apparently had sufficient dolomite or calcite to produce such an effect. Thus a basinwide study of exchangeable cations to test their effect on gas production, as we had originally intended, is impossible. Also, the shale appears to be uniformly calcareous, perhaps having a small but ubiquitous amount of calcite cement.

INTRODUCTION

Most clay minerals, and hence most shales, exhibit the phenomenon of ion-exchange. This refers to the exchange of an ion held by an electrical charge near the surface of a mineral for one in a solution to which the mineral is exposed. For clays, exchange of cations is the most important reaction. Grim (1968, p. 193) states that the most important cause for cation exchange is substitution within the lattice structure. For example, substitution of Al^{+3} for Si^{+4} in the tetrahedral sheet (fig. 1) or of Mg^{+2} for Al^{+3} in the octahedral sheet, results in a lattice with an unbalanced charge. This net negative charge is balanced by loosely held (exchangeable) cations.

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Exchangeable cations
nH$_2$O

○ Oxygens   (OH) Hydroxyls   ● Aluminum, iron, magnesium
○ and ● Silicon, occasionally aluminum
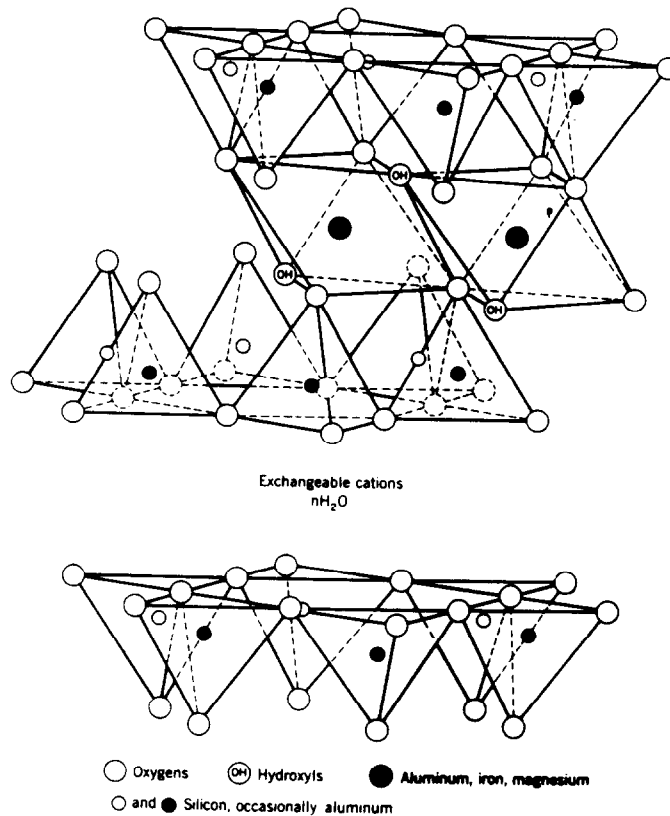
FIGURE 1. - Diagrammatic sketch of smectite structure showing position
            of exchangeable cations (Grim, 1968, p. 79).

The total number of exchangeable cations, or the cation exchange capacity
(CEC), is controlled largely by mineralogy and surface area, smectites having
the highest CEC, illites lower, and kaolinites the lowest. The type of ion
held in exchange positions is, however, more a function of the composition
of the fluids to which the clay has been exposed.

Exchangeable cations are of potential importance in the Eastern Gas
Shale Project because they affect the engineering properties of shales, and
these, in turn, may affect gas production. These effects are of two kinds:
response of the shale to fluids used in drilling or stimulation, and
ability of the shale to transmit fluids. Both are governed essentially by
the ratio of Na^+ to Ca^{++} plus Mg^{++} in exchange sites. Exchangeable K^+ is
not reported to have any significant effect.

Clays exhibit differences in fabric, ranging from loose, open structures
to compact, stable ones. Clays with open fabrics are particularly undesirable
in construction because of their lower strengths (Mitchell, 1976, pp. 208-221),
and in oil well drilling because they may expand to plug the pore spaces in
sandstones (van Olphen, 1963, p. 127). The fabric is controlled primarily
by salinity, high salinities producing closed, stable structures, but also
by the exchangeable cation, Na^+ favoring more open structures. Therefore,

use of a low salinity or high Na^+ drilling mud or fracturing fluid can lead to formation damage. Furthermore, use of water in fracturing a shale which has a high concentration of exchangeable Na^+ could lead to problems. O'Brien and Chenevert (1973) have described shale problems of this type, and suggest the use of high potassium fluids can overcome these problems in illite-rich rocks such as the Devonian shales.

In the same way, exchangeable cations in the shale may affect its ability to transmit fluids. Figure 1 shows that high Na^+ illites have a lower permeability than those high in Ca^{++}. Furthermore, the exchange cation may well affect the ability of a clay particle to absorb a neutral organic molecule, such as methane, although little work has been done on illites (Grim, 1968, pp. 378-381). Accordingly, we felt that it was desirable to investigate the proportions of the various exchangeable cations found in the black shale, and their areal distribution.
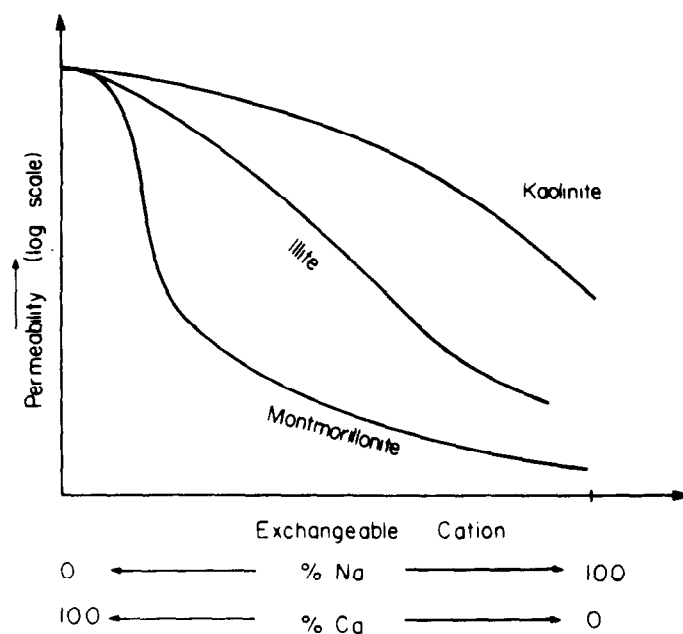
FIGURE 2. - Effect of exchange cation on permeability (Yong and Warkentin, 1975, Fig. 2.20).

METHODS

The approach used in this study was essentially that of Spears (1973). Duplicate shale samples were ground to 100-200 mesh. 200 mg of each were washed twice with distilled water, then reacted with 14 ml of 1 M NH_4 acetate for 48 hours. The resulting solution was centrifuged for a few minutes to separate the clays from the solution, which was then withdrawn for atomic absorption analysis. For this we used a Perkin-Elmer 403 spectrophotometer with hollow cathode lamps. Duplicate values were normally quite close ($\pm 3\%$), except for a few Na^+ analyses in which one sample would

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be much higher than normal, an effect we attribute to contaminated glassware, because we have noticed that very careful handling of glassware is necessary to achieve uniformly low Na^+ blanks. Such samples were not included in the data presented.

The clay was washed again, then reexchanged with 0.5 M $BaCL_2$, and the released NH_4^+ measured with an Orion NH_4^+ electrode to get an estimate of the exchange capacity. Duplicates agreed within ±6 percent. Ba^{++} is a less efficient ion-exchanger than NH_4^+, which is used in the first exchange because of its ability to displace other ions, so that this technique underestimates the CEC. Based on curves in Grim (1968, p. 219), this concentration of Ba^{++} should recover about 60 percent of the NH_4^+, but the results show that only 40 percent was recovered in our samples (Table 1, last column).

The samples used were from cores from a group of four closely spaced wells in Richland County, Ohio, and a single well in Perry County, Kentucky (Table 2).

RESULTS AND DISCUSSION

In almost all of the samples studied, the amount of exchangeable Ca^{++} plus Mg^{++} is much greater than Na^+ (Table 1). Thus we expect there to be no problems of fluid compatibility related to exchangeable Na^+. In addition, there is no obvious stratigraphic trend in the data (Fig. 3).

We encountered an unexpected analytical difficulty, however. Even small amounts of calcite in a sample drastically affect the exchangeable cations. This was shown by adding ground calcite to selected samples, which resulted in sharp increases in the measured exchangeable Ca^{++}, decreases in Mg^{++}, and variable behavior of Na^+ (Table 3). That such an effect is important in our shale samples can be seen in Figure 2 where there are several extremely high Ca^{++} samples with correspondingly low Na^+. Some, especially towards the base of the section, show parallel trends of high Mg^{++} and Ca^{++}, suggesting that dolomite also interferes.

It can be seen from Table 3 that changing the exchanging cation from NH_4^+ to Ba^{++} or K^+ does not overcome this problem. Furthermore, the NH_4^+ source in this experiment was NH_4Cl, so the acetate anion is not causing the problem. Several other effects can be noted. For instance, the cation exchange capacity (CEC) decreases significantly in the $CaCO_3$-containing samples. Apparently Ca^{++} from the $CaCO_3$ is also acting as an ion-exchanger, taking up sites that would normally be occupied by NH_4^+. The decrease in the other exchangeable cations, particularly Mg^{++}, suggests that they are being adsorbed by the calcite surfaces once they have been released by the clays. Both of these effects suggest that this calcite interference cannot be corrected simply by measuring the CEC and obtaining the value for exchangeable Ca^{++} by subtracting the values for Mg^{++}, K^+, and Na^+, as has been suggested by Bischoff, et al. (1975).

Another possible way to overcome this interference would be to separate the clays from the carbonates. However, any selective dissolution of the carbonates would exchange most of the cations. Dispersing the clays with an agent such as Na^+-phosphate (calgon) in order to separate the carbonates by settling would also alter the exchangeable cations. Further, it seems likely that the clay and carbonate may be of about the same size.
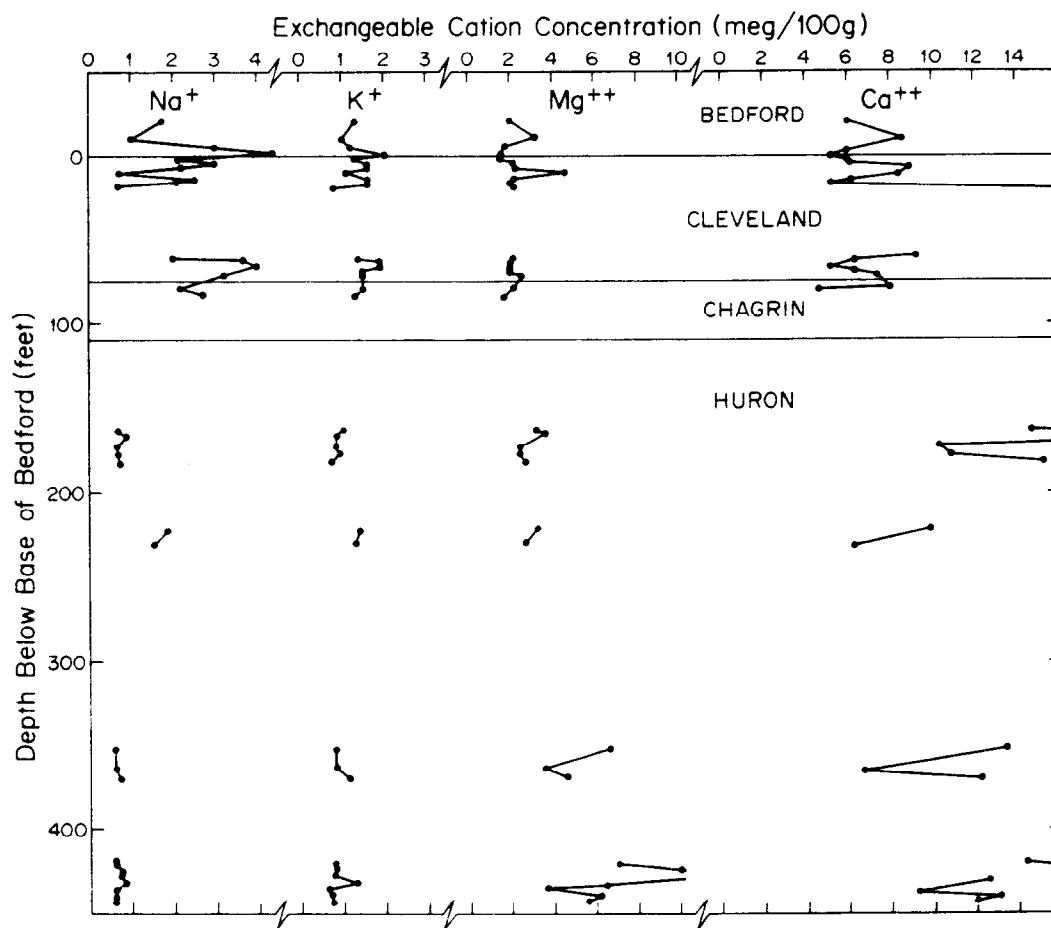
Figure 5. --Distribution of Exchangeable Cations in the Ohio
Shale, Richland County, Ohio

Our inability to overcome this interference from two common minerals, calcite and dolomite, leads us to conclude that a regional stratigraphic study of exchangeable cations would not be worthwhile.

It is also reasonable to ask whether this interference invalidates our conclusion about the predominance of exchangeable Ca^{++} over Na^+. On a practical level the answer to this question is no; whatever the source of the Ca^{++} released by the exchange process, it will still suppress the action of Na^+ on the clay fabric. However, the interference by carbonate minerals probably makes determining the true exchangeable cation population impossible. Carbonate contamination in this type of measurement can be detected by comparing CEC^2 (the exchange capacity measured with the NH_4^+-electrode) to CEC^1 (the apparent cation exchange capacity calculated by summing the milliequivalents of charge contributed by each cation). As mentioned, when Ba^{++} is used to re-exchange the NH_4^+, the ratio of these two quantities should be about .60. In a study of Pennsylvanian shales, Ulmschneider (1977) found this ratio for carbonate-free samples, but carbonate-containing samples were much lower. The Devonian samples analyzed in this study average only .40 for CEC^2/CEC^1 even when very high Ca^{++} samples are neglected. The highest value found was only .53. This behavior suggests that most, if not all, of the samples studied contain small amounts of a carbonate mineral, making an accurate measurement of the exchangeable cations impossible. If this were true, it suggests the interesting possibility that the Devonian shale is almost uniformly calcareous, perhaps having a small amount of calcite cement.

Keeping this limitation in mind, it is possible to arrive at an average population of exchangeable cations for the shale.

$$Na^+ = 2.75 \text{ meq/100 g} \qquad CEC^2 = 12.80 \text{ meq/100 g}$$
$$K^+ = 1.54 \qquad\qquad CEC^1 = 5.31$$
$$Mg^{++} = 2.05 \qquad\qquad CEC^2/CEC^1 = .41$$
$$Ca^{++} = 6.46$$
$$Mg^{++}/Ca^{++} = .32$$

This value of Mg^{++}/Ca^{++} is well within the range for non-marine samples (calcite-free marine shales usually have $Mg^{++}/Ca^{++} > .80$, Ulmschneider, 1977), again confirming that we are really measuring the exchangeable cations in a clay-carbonate system.

TABLE 1. - EXCHANGEABLE CATIONS IN DEVONIAN SHALES
(locations in Table 2)

Well	Depth Below Top Ohio Shale (feet)	Exchangeable Cations (meq/100g) Na^+	K^+	Mg^{++}	Ca^{++}	CEC^1	CEC^2	$\dfrac{CEC^2}{CEC^1}$
Richland County, Ohio								
E	+20	1.68	1.33	1.96	5.96	10.93	5.05	.47
E	+ 9	.98	.98	5.32	8.68	15.96	3.80	.24
K3	+ 2.8	3.01	1.19	1.82	5.88	11.90	5.25	.44
K3	+ 0.6	4.41	2.03	1.68	5.32	13.44	5.15	.38
K3	2	2.10	1.33	1.54	6.16	11.13	5.10	.46
E	4	3.01	1.61	2.10	6.30	13.02	6.00	.46
E	6	2.17	1.61	2.24	9.10	15.12	5.60	.37
K3	9.8	.70	1.05	4.62	8.40	14.77	5.10	.35
K3	13.6	2.10	1.61	2.24	6.30	12.25	5.25	.43
E	14	2.45	1.61	1.95	5.32	11.34	5.10	.45
E	17	.70	.84	2.24	30.80	34.58	5.00	.14
K2	61.5	1.96	1.40	2.24	9.24	14.84	5.55	.37
K2	63.5	3.71	1.89	1.96	6.30	13.86	5.20	.38
K2	66.5	3.92	1.89	1.96	5.32	13.09	5.25	.40
K2	69.5	3.92	1.54	1.96	6.30	13.72	5.40	.39
K2	71.5	3.22	1.47	2.52	7.42	14.63	5.75	.39
K2	79.5	2.17	1.54	2.24	7.98	13.93	5.25	.38
K2	80.5	2.66	1.26	1.68	4.34	9.94	5.25	.53
E	164	.70	.98	3.22	14.70	19.60	4.70	.24
E	166	.84	.84	3.64	30.10	35.42	3.60	.10
E	172	.63	.84	2.38	10.22	14.07	4.70	.34
E	178	.63	.91	2.38	10.78	14.70	4.30	.29
E	183	.63	.77	2.66	15.12	19.18	4.50	.23
R	223	1.82	1.40	3.64	9.80	16.66	5.15	.31
R	231	1.54	1.26	2.66	6.16	11.62	4.80	.41
R	353	.56	.84	6.72	13.44	21.56	3.30	.15
R	365	.56	.84	3.50	6.58	11.48	4.10	.36
R	370	.63	1.12	5.46	12.18	19.39	3.90	.20
K2	419.3	.63	.77	7.14	14.28	22.82	2.30	.10
K2	425.7	.70	.77	9.94	18.62	20.72	1.80	.09
K2	428.4	.70	.77	13.30	23.24	38.01	1.55	.04
K2	431.4	.84	1.33	6.44	12.60	21.21	3.90	.18
K2	438.8	.56	.63	3.78	9.24	14.21	3.00	.21
K2	440.5	.56	.70	6.16	13.02	20.44	3.00	.15
K2	442.5	.56	.70	5.60	11.90	18.76	2.90	.15
Perry County, Kentucky								
C	12	.70	1.19	3.64	6.44	11.97	3.40	.28
C	45	.56	1.12	3.92	7.56	13.16	3.40	.26
C	80	1.54	1.68	2.66	6.16	12.04	5.50	.46
C	178	.77	1.47	4.48	8.68	15.40	4.70	.31
C	295	.49	1.05	3.36	5.32	10.22	2.05	.20
C	305	.56	1.05	5.74	7.98	15.33	3.00	.20

CEC^1 = sum of cations (meq/100g)
CEC^2 = ηH_4^+ electrode determination (meq/100g)

TABLE 2. –Well locations

1. Ohio Wells (all Richland County, Section 30)

Well	Cored Interval	Top of Ohio Shale (γ-Ray)

Jerry Moore, Inc. No. 1 K. Egner
  Plymouth Twp.
  62' FNL & 1335' FWL, NW/4
  Permit No. 526
	330–367
	514–533
		350

Jerry Moore, Inc. No. 1 H. N. Romog
  Plymouth Twp.
  706' FNL & 196' FWL, SW/4
  Permit No. 523
	553–561
	678–708
		330

Great Basins Petrol. No. 3 Kocheiser
  Washington Twp.
  950' FNL & 490' FEL, NE/4
  Permit No. 528
	607–624	610

Great Basins Petrol. No. 2 Kocheiser
  Washington Twp.
  422' FSL & 550' FEL, SE/4
  Permit No. 527
	665–690
	1021–1046
		604

2. Kentucky Well (Perry County)

Well	Cored Interval	Top of Ohio Shale (γ-Ray)

Kentucky-West Va. No. 7239 N. Combs
  19-K-77
  1690' FNL & 325' FWL
  Permit No. 28982
	2369–2708	2369

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TABLE 3. – EFFECT OF CaCO$_3$ ON MEASUREMENT OF

EXCHANGEABLE CATIONS

Sample # & Exchange Cation	Percent CaCO$_3$ Added	Exchanged cations (milliequivalents/100 g shale)						
		Mg^{++}	Ca^{++}	Mg^{++}/Ca^{++}	Na$^+$	K$^+$	CEC^1	CEC^2
P-5 Ba^{++}	0	.50	1.16	.43	.21	.66	2.53	--
	2.5	.30	12.18	.02	.42	.76	13.66	--
	5.0	.26	12.18	.02	.42	.82		
	10.0	.30	12.60	.02	.42	.77		
P-5 K$^+$	0	.44	.546	.80	.28	--		2.24
	2.5	.028	3.30	.008	.35	--		.98
	5.0	.042	3.34	.012	.35	--		
	10.0	.042	3.30	.013	.14	--		
P-5 NH$_4^+$	0	.50	1.16	.43	.74	0	2.40	2.87
	2.5	.54	26.6	.02	.74	0	27.88	1.96
	5.0	.60	32.2	.02	.35	0		
	10.0	.62	37.8	.02	.70	0		
M-24 Ba^{++}	0	5.60	6.22	.90	.28	1.02	13.12	--
	2.5	3.92	13.80	.28	.63	1.04	19.39	--
	5.0	3.54	16.10	.21	.49	.88		
	10.0	3.14	18.90	.17	.49	.93		
M-24 K$^+$	0	4.90	2.32	2.11	.56	--		6.72
	2.5	1.66	8.46	.20	.35	--		4.62
	5.0	1.48	9.38	.18	.36	--		
	10.0	1.32	8.50	.16	.42	--		
M-24 NH$_4^+$	0	5.16	3.96	1.30	.28	.20	9.60	6.30
	2.5	4.04	32.90	.12	.63	.23	37.80	2.45
	5.0	4.08	37.10	.11	.42	.35		
	10.0	3.84	42.70	.09	.70	.29		
M-29 Ba^{++}	0	1.32	1.16	1.14	.21	.82	3.51	--
	2.5	.64	11.32	.06	.35	.95	13.26	--
	5.0	.58	13.04	.04	.42	.95		
	10.0	.56	12.76	.04	.35	.99		
M-29 K$^+$	0	1.18	.546	2.16	.56	--		2.24
	2.5	.070	3.90	.02	.42	--		.98
	5.0	.070	3.90	.02	.42	--		
	10.0	.070	3.72	.02	.42	--		
M-29 NH$_4^+$	0	1.28	1.374	1.00	.49	0	3.04	2.66
	2.5	1.04	25.20	.04	.21	.16	26.61	1.33
	5.0	1.06	31.50	.03	.56	.13		
	10.0	1.08	35.00	.03	.63	.18		

[1]Sum of exchanged cations

[2]Amount of exchange cation recovered by treating with NH$_4^+$ (K$^+$ - clay) or K$^+$(NH$_4^+$ - clay).

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